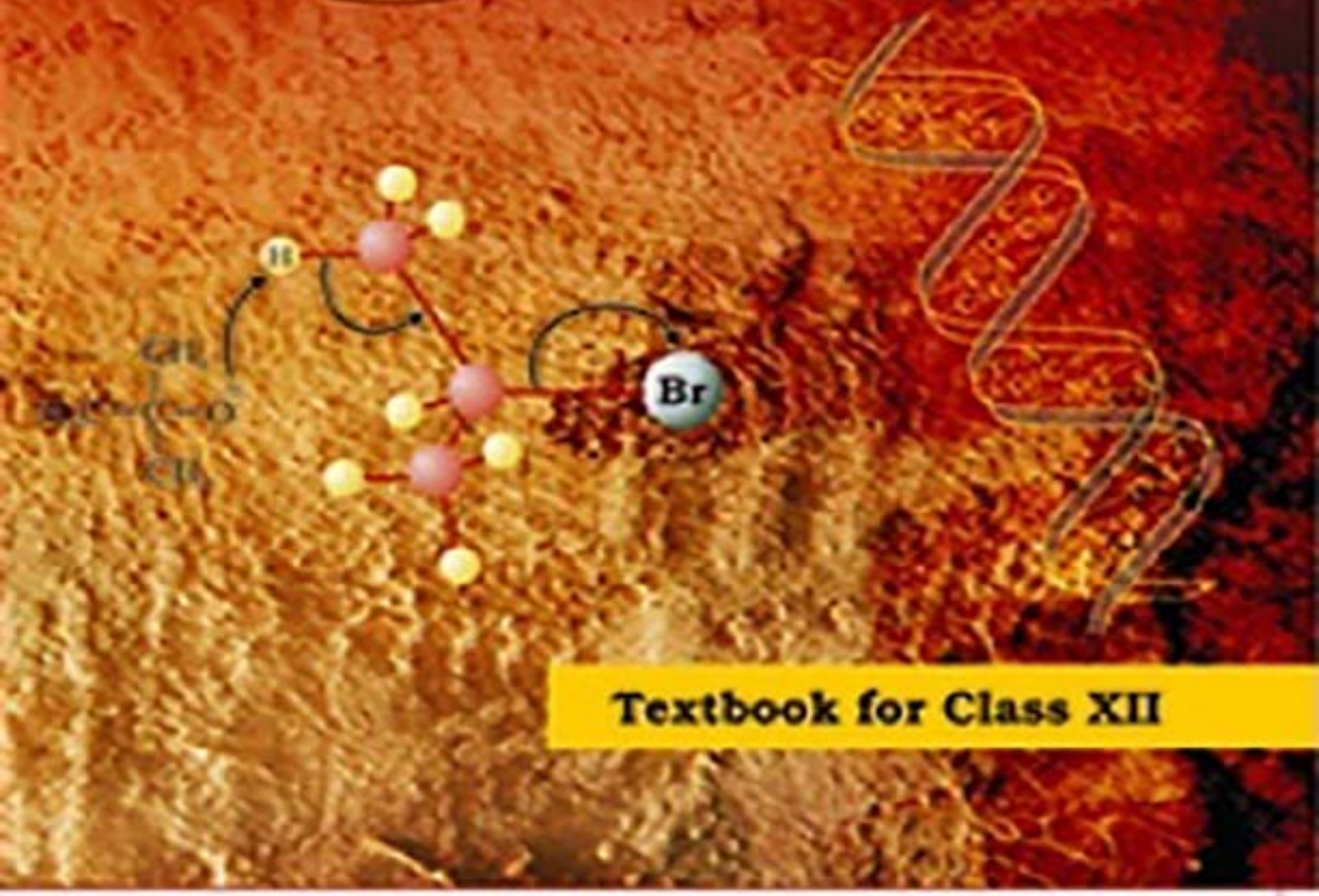
Chemistry

Part II



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Unit

10

Haloalkanes and Haloarenes

Objectives

After studying this Unit, you will be able to

- name haloalkanes and haloarenes according to the IUPAC system of nomenclature from their given structures;
- describe the reactions involved in the preparation of haloalkanes and haloarenes and understand various reactions that they undergo;
- correlate the structures of haloalkanes and haloarenes with various types of reactions;
- use stereochemistry as a tool for understanding the reaction mechanism;
- appreciate the applications of organo-metallic compounds;
- highlight the environmental effects of polyhalogen compounds.

Halogenated compounds persist in the environment due to their resistance to breakdown by soil bacteria.

The replacement of hydrogen atom(s) in a hydrocarbon, aliphatic or aromatic, by halogen atom(s) results in the formation of alkyl halide (haloalkane) and aryl halide (haloarene), respectively. Haloalkanes contain halogen atom(s) attached to the sp^3 hybridised carbon atom of an alkyl group whereas haloarenes contain halogen atom(s) attached to sp^2 hybridised carbon atom(s) of an aryl group. Many halogen containing organic compounds occur in nature and some of these are clinically useful. These classes of compounds find wide applications in industry as well as in day-to-day life. They are used as solvents for relatively non-polar compounds and as starting materials for the synthesis of wide range of organic compounds. Chlorine containing antibiotic, *chloramphenicol,* produced by soil microorganisms is very effective for the treatment of typhoid fever. Our body produces iodine containing hormone, *thyroxine,* the deficiency of which causes a disease called *goiter*. Synthetic halogen compounds, *viz.* chloroquine is used for the treatment of malaria; halothane is used as an anaesthetic during surgery. Certain fully fluorinated compounds are being considered as potential blood substitutes in surgery.

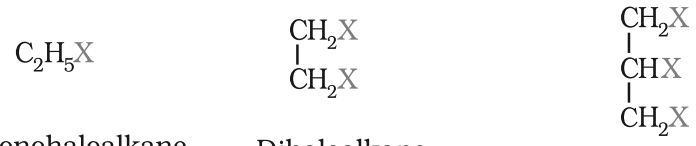
In this Unit, you will study the important methods of preparation, physical and chemical properties and uses of organohalogen compounds.

10.1 Classification

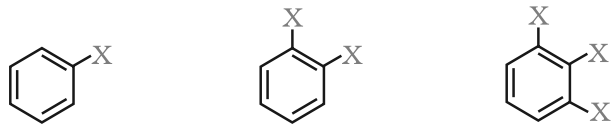
Haloalkanes and haloarenes may be classified as follows:

10.1.1 On the Basis of Number of Halogen Atoms

These may be classified as mono, di, or polyhalogen (tri-,tetra-, etc.) compounds depending on whether they contain one, two or more halogen atoms in their structures. For example,



Monohaloalkane Dihaloalkane Trihaloalkane



Monohaloarene Dihaloarene Trihaloarene

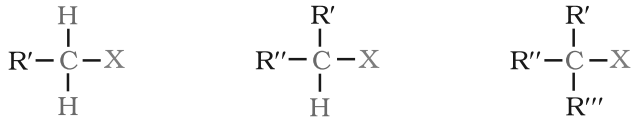
Monohalocompounds may further be classified according to the hybridisation of the carbon atom to which the halogen is bonded, as discussed below.

10.1.2 Compounds Containing sp^3 C—X Bond (X= F, Cl, Br, I)

This class includes

(a) Alkyl halides or haloalkanes (R—X)

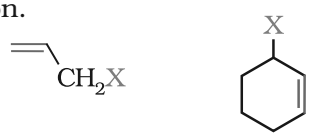
In alkyl halides, the halogen atom is bonded to an alkyl group (R). They form a homologous series represented by $C_nH_{2n+1}X$. They are further classified as primary, secondary or tertiary according to the nature of carbon to which halogen is attached.



Primary (1°) Secondary (2°) Tertiary (3°)

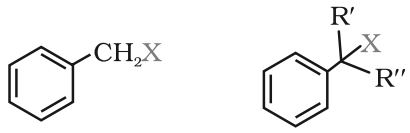
(b) Allylic halides

These are the compounds in which the halogen atom is bonded to an sp^3-hybridised carbon atom next to carbon-carbon double bond (C=C) *i.e.* to an allylic carbon.



(c) Benzylic halides

These are the compounds in which the halogen atom is bonded to an sp^3-hybridised carbon atom next to an aromatic ring.



(1°) $R' = CH_3$, $R'' = H$ (2°)

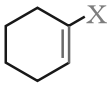
$R' = R'' = CH_3$ (3°)

10.1.3 Compounds Containing sp^2 C—X Bond

This class includes:

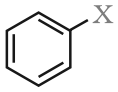
(a) Vinylic halides

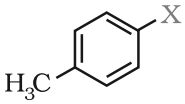
These are the compounds in which the halogen atom is bonded to an sp^2-hybridised carbon atom of a carbon-carbon double bond (C = C).



(b) Aryl halides

These are the compounds in which the halogen atom is bonded to the sp^2-hybridised carbon atom of an aromatic ring.

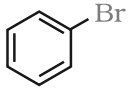
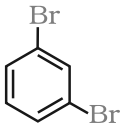
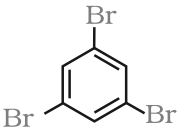




10.2 Nomenclature

Having learnt the classification of halogenated compounds, let us now learn how these are named. The common names of alkyl halides are derived by naming the alkyl group followed by the halide. Alkyl halides are named as halosubstituted hydrocarbons in the IUPAC system of nomenclature. Haloarenes are the common as well as IUPAC names of aryl halides. For dihalogen derivatives, the prefixes *o*-, *m*-, *p*- are used in common system but in IUPAC system, the numerals 1,2; 1,3 and 1,4 are used.

	$CH_3CH_2CH_2Br$	$H_3C–\underset{\underset{Cl}{\vert}}{CH}–CH_3$	$H_3C–\overset{\overset{CH_3}{\vert}}{CH}–CH_2Cl$
Common name:	n-Propyl bromide	Isopropyl chloride	Isobutyl chloride
IUPAC name:	1-Bromopropane	2-Chloropropane	1-Chloro-2-methylpropane

			
Common name:	Bromobenzene	*m*-Dibromobenzene	*sym*-Tribromobenzene
IUPAC name:	Bromobenzene	1,3-Dibromobenzene	1,3,5-Tribromobenzene

	$H_3C–\overset{\overset{CH_3}{\vert}}{\underset{\underset{CH_3}{\vert}}{C}}–CH_2–Cl$	$H_3C–\underset{\underset{Br}{\vert}}{CH}–CH_3$
IUPAC name:	1-Chloro-2,2-dimethylpropane	2-Bromopropane

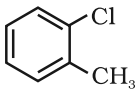
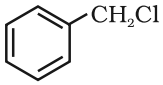
The dihaloalkanes having the same type of halogen atoms are named as alkylidene or alkylene dihalides. The dihalo-compounds having same type of halogen atoms are further classified as geminal halides (halogen atoms are present on the same carbon atom) and vicinal halides (halogen atoms are present on the adjacent carbon atoms). In common name system, *gem*-dihalides are named as alkylidene halides and *vic*-dihalides

are named as alkylene dihalides. In IUPAC system, they are named as dihaloalkanes.

	$H_3C-CHCl_2$	$H_2C(Cl)-CH_2(Cl)$
Common name:	Ethylidene chloride (*gem*-dihalide)	Ethylene dichloride (*vic-dihalide*)
IUPAC name:	1, 1-Dichloroethane	1, 2-Dichloroethane

Some common examples of halocompounds are mentioned in Table 10.1.

Table 10.1: Common and IUPAC names of some Halides

Structure	Common name	IUPAC name
$CH_3CH_2CH(Cl)CH_3$	sec-Butyl chloride	2-Chlorobutane
$(CH_3)_3CCH_2Br$	neo-Pentyl bromide	1-Bromo-2,2-dimethylpropane
$(CH_3)_3CBr$	tert-Butyl bromide	2-Bromo-2-methylpropane
$CH_2 = CHCl$	Vinyl chloride	Chloroethene
$CH_2 = CHCH_2Br$	Allyl bromide	3-Bromopropene
	*o*-Chlorotoluene	1-Chloro-2-methylbenzene or 2-Chlorotoluene
	Benzyl chloride	Chlorophenylmethane
CH_2Cl_2	Methylene chloride	Dichloromethane
$CHCl_3$	Chloroform	Trichloromethane
$CHBr_3$	Bromoform	Tribromomethane
CCl_4	Carbon tetrachloride	Tetrachloromethane
$CH_3CH_2CH_2F$	n-Propyl fluoride	1-Fluoropropane

Example 10.1 Draw the structures of all the eight structural isomers that have the molecular formula $C_5H_{11}Br$. Name each isomer according to IUPAC system and classify them as primary, secondary or tertiary bromide.

Solution

$CH_3CH_2CH_2CH_2CH_2Br$	1-Bromopentane (1°)
$CH_3CH_2CH_2CH(Br)CH_3$	2-Bromopentane(2°)
$CH_3CH_2CH(Br)CH_2CH_3$	3-Bromopentane (2°)
$(CH_3)_2CHCH_2CH_2Br$	1-Bromo-3-methylbutane (1°)

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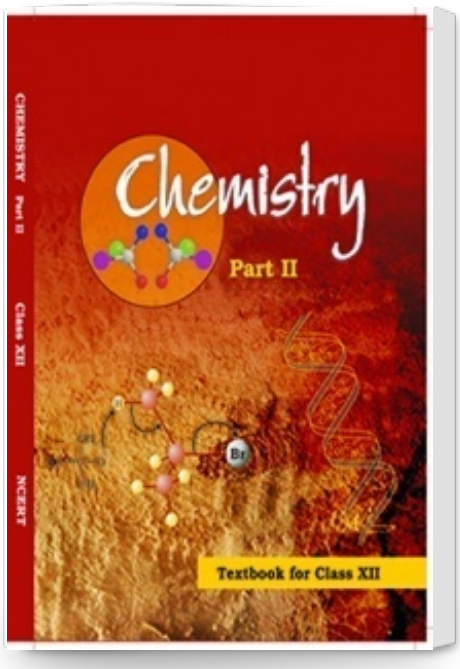

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